

Effects of local heating and premelting in the terminal part of the e^+ track

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A. Introduction

The terminal part of the e^+ track (the positron blob) is formed during ionization slowing down and subsequent ion-electron recombinations produced by a positron. It releases up to 1 keV of energy, which is converted into heat within few picoseconds. If a bulk temperature of a medium is below, but close enough to its melting point, some region of a substance may melt, yielding a peculiar temperature dependence of the lifetime (LT) spectra.

We have estimated properties of the molten region with a help of macroscopic heat conduction equation and suggested a model describing temperature dependence of the ortho-positronium lifetime in frozen methanol, ethanol, butanol and water close to their melting points.

B. General equations. Homogeneous medium

In a homogeneous medium the heat conductivity equation for the e^+ blob looks as follows:

$$c_p \rho \frac{\partial T(r, t)}{\partial t} = \text{div}(\lambda \nabla T) + q_+(r, t), \quad T(r, t = 0) = T_{bulk}. \quad (1)$$

Here $T(r, t)$ is the local temperature, T_{bulk} is the bulk temperature of the medium, c_p is its specific heat capacity, ρ is the density, λ is the thermal conductivity. The second term in the RHS describes energy release by the positron when it creates the blob: $q_+(r, t) \approx W_{blob} G(r, a) f(t, \tau)$, where $W_{blob} \approx 1$ keV is the blob formation energy, $G(r, a) = \frac{e^{-r^2/a^2}}{\pi^{3/2} a^3}$ describes spatial distribution of the released energy (a is about tens of Å) and $f(t, \tau)$ its temporal distribution (here τ is the typical time of ion-electron recombination and should be of the order of 1-10 ps). We adopted that $f(t, \tau) = \exp\left(-\frac{(t-1 \text{ ps})^2}{2\tau^2}\right) / (\sqrt{2\pi}\tau)$, where $\tau = 0.3$ ps. Since a system is simultaneously solid and liquid we used the following method for obtaining a numerical solution of Eq. (1) [1]. An additional contribution to $c_p(T)$ was used to simulate a presence of the latent heat of melting (q_m). It is non-zero only in a small temperature interval ΔT around T_m (the melting point temperature) and its integral over temperature in ΔT range should be equal to q_m . The value of ΔT (phase transition width) was arbitrarily fixed to 0.25 K. An additional contribution to c_p related with the latent heat was simulated by a Gaussian T -dependent function. Dependencies of $c_p(T)$ as well as $\lambda(T)$ and $\rho(T)$ are described by smooth functions over T as proposed in [1]. Thermodynamical

properties of methanol, ethanol, butanol and water used in present work are taken from [2–5].

C. Estimated properties of molten region

Temperature profiles $T(r, t)$ were calculated numerically for $0 < r < 200 \text{ \AA}$ and $0 < t < 1 \text{ ns}$. Eq. (1) was solved as 1-D problem with boundary conditions $T(r = 200 \text{ \AA}) = T_{\text{bulk}}$ with a help of PDEPE solver from **Matlab**. The phase of medium is deduced from the temperature of each spatial point, which can be higher than $T_m + \Delta T$ (liquid phase) or lower than $T_m - \Delta T$ (solid phase).

Fig. 1 displays the maximum radius of the molten region, R_{max} , vs. T_{bulk} and the lifetime t_{max} of the molten region (at $t > t_{\text{max}}$ temperature of an any point of the medium is below $T_m + \Delta T$).

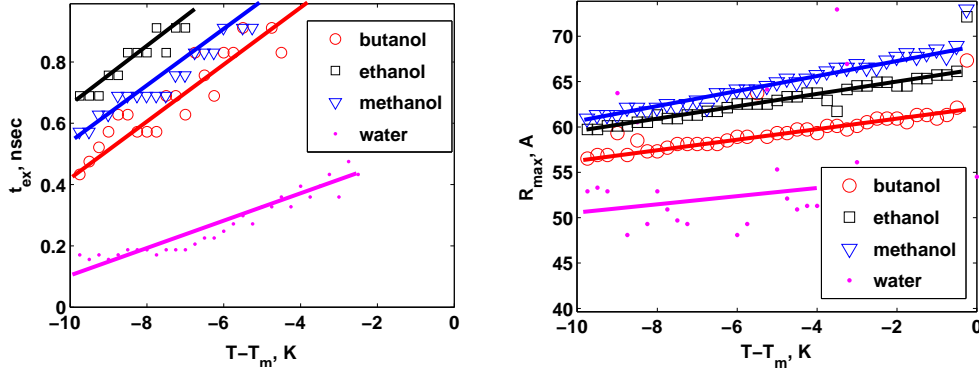


FIG. 1: Lifetime of the molten region t_m (left) and its radius R_m (right) for methanol, ethanol, butanol and water are displayed as a function of $T_b - T_m$.

D. Experimental data.

Positron annihilation lifetime spectra in alcohols and in water were measured in Maria Curie-Skłodowska University. Each lifetime spectrum was deconvoluted into 3 exponents by means of LT 92 program. The data were processed at a fixed ratio of ortho-Ps to para-Ps intensities equal to 3:1. Fig. 2 displays temperature variation of the lifetime of the long-lived component of LT spectra vs. T close to the melting points.

For alcohols one can observe a noticeable temperature shift between the beginning of $\tau_3(T)$ plateau and the melting point. For description of $\tau_3(T)$ dependencies the following

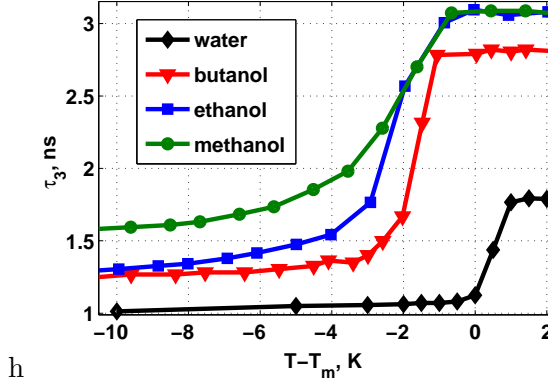


FIG. 2: Experimental data for the lifetime of ortho-positronium component in alcohols and water. Temperature T of investigated medium is plotted relatively to T_m of certain substance. model is proposed.

E. Theoretical model.

Let us divide a space-time evolution of the Ps into two subsequent stages, namely, its formation and annihilation. The first stage is initiated by a heat generation during e^+ ionization slowing down, when it forms a terminal blob. As a result, intrablob region may melt, so therein formation of the Ps bubble is possible. Typical duration of the first stage may be estimated as about $t_{max} \sim 10$ ps, so annihilation may be neglected.

When temperature of the medium approaches to the melting point, concentration of free volume elements (FVE; or vacancy-like defects) rise extensively. These FVE trap Ps and yield its typical lifetime as about $\tau_S \approx 1.2$ - 1.5 ps.

Frozen phase usually consists of domains which are disordered in a different extent (local density fluctuations, intercrystalline boundaries and so on). Local inhomogeneity of the medium leads to smearing of its melting temperature. It is the reason of the *premelting* effect (an appearance of some molten domains when T_{bulk} is slightly below T_m). Hence the formation of the Ps bubble state may occur in these premelted regions.

Let us consider Ps formation during the first stage in terms of concentrations of different Ps states, namely, mobile quasi-free positronium qf-Ps, $c_{qf}(r, t)$, Ps trapped in FVE of a solid phase, c_v , and Ps bubble state, c_b , formed in the molten region of the blob and in the premelted domains. Evolution of these states is described by the following set of kinetic

equations:

$$\frac{\partial c_{qf}(r, t)}{\partial t} = D\Delta c_{qf} - (\lambda_v + \lambda_b)c_{qf}, \quad \frac{\partial c_v(r, t)}{\partial t} = \lambda_v c_{qf}, \quad \frac{\partial c_b(r, t)}{\partial t} = \lambda_b c_{qf}. \quad (2)$$

Here $D \sim 0.03 \text{ cm}^2/\text{sec}$ is the diffusion coefficient of qf-Ps (we assume that the mean free path of Ps transport is about its de Broglie wave length and qf-Ps velocity is the thermal one), $\lambda_v(T)$ and $\lambda_b(T)$ are Ps trapping rates by FVE and premelted regions.

At $t = 0$ we have qf-Ps only. We adopt that its initial distribution is approximately Gaussian and that it remains Gaussian later at any t , namely, $c_{qf}(r, t) = n_{qf}(t)G(r, t, D)$, where $G(r, t, D) = \frac{\exp(-r^2/(a^2+4Dt))}{[\pi(a^2+4Dt)]^{3/2}}$. Hence $n_{qf}(t) = P_{\text{qf-Ps}}e^{-(\lambda_v+\lambda_b)t}$, where $P_{\text{qf-Ps}}$ is the formation probability of qf-Ps. Distributions c_v and c_b can be found from (2) and are equal to $c_{v,b}(r, t) = \int_0^t dt' \lambda_{v,b} c_{qf}(r, t')$.

The first stage is terminated by a formation of the molten region with the radius, attaining its maximal value $R_m(T_{\text{bulk}})$ at t_{max} . By this time the fraction f_m of Ps atoms in premelted regions (i.e. in a liquid phase) is $f_m = \int_{r < R_m} (c_{qf}(r, t_{\text{max}}) + c_v(r, t_{\text{max}}) + c_b(r, t_{\text{max}})) d^3r$. By the time $t_{\text{max}} \sim 10 \text{ ps}$ all these Ps states turn out to be in a bubble state (Ps bubble formation time is about 10 ps as well [6]). After subsequent freezing of the molten region we assume that the bubble state does not collapse. Cavity survives after freezing with the Ps inside, so ortho-Ps lifetime remains the same.

We assume that all qf-Ps atoms outside the molten region, remaining quasi-free by the time t_{max} , become trapped shortly by FVE or premelted regions (n_v or n_b) in proportion to $\lambda_v/(\lambda_v + \lambda_b)$ and $\lambda_b/(\lambda_v + \lambda_b)$. Therefore, total formation probability P_{Ps} of the Ps bubble state arises not only from the molten central region of the blob, but also from premelted domains, so that $P_{\text{Ps}} = f_m + \int_{r > R_m} \left[c_b(r, t_{\text{max}}) + \frac{\lambda_b}{\lambda_v + \lambda_b} c_{qf}(r, t_{\text{max}}) \right] d^3r$.

Annihilation of the free positrons and Ps states occurs on the second stage at $t > t_{\text{max}} \approx 0$. We assume that formation of para- and ortho-Ps spin states takes place in a conventional 1:3 proportion (possible influence of intratrack chemical reactions which may change this ratio is neglected). Let n_{pPs} (n_{oPs}) be the fraction of para-Ps (ortho-Ps) formed in a bubble state. Following equations allow to calculate a shape of LT spectrum according to proposed model:

$$\begin{aligned} \dot{n}_+ &= -\lambda_+ n_+, & n_+(0) &= 1 - P_{\text{qf-Ps}}; & \dot{n}_{\text{oPs}} &= -\lambda_{\text{po}} n_{\text{oPs}}, & n_{\text{oPs}}(0) &= 3P_{\text{Ps}}/4; \\ \dot{n}_{\text{pPs}} &= -\lambda_{\text{pPs}} n_{\text{pPs}}, & n_{\text{pPs}}(0) &= \frac{P_{\text{Ps}}}{4} + \frac{1}{4} \int_{r > R_m} \left(c_v(r, t_{\text{max}}) + \frac{\lambda_v}{\lambda_v + \lambda_b} c_{qf}(r, t_{\text{max}}) \right) d^3r; \end{aligned}$$

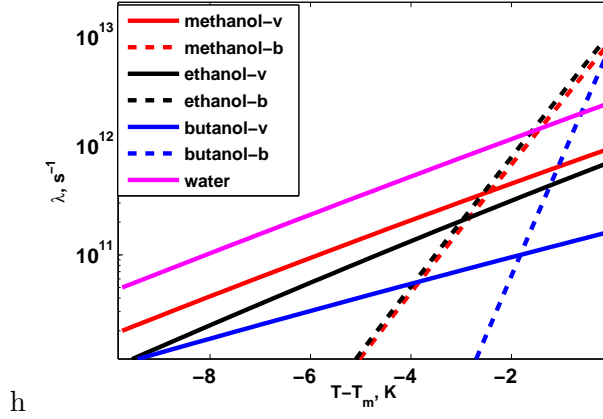


FIG. 3: Temperature dependencies of trapping rates λ_v (solid lines) and λ_b (dashed lines) for methanol, ethanol, butanol and water. Temperature is given with respect to melting point of each substance.

$$\dot{n}_v = -\lambda_S n_v, \quad n_v(0) = \frac{3}{4} \int_{r>R_m} \left(c_v(r, t_{max}) + \frac{\lambda_v}{\lambda_v + \lambda_b} c_{qf}(r, t_{max}) \right) d^3r.$$

These equations yield a four-component LT spectrum, where $\lambda_+ \approx 2 \text{ ns}^{-1}$ is the free e^+ annihilation rate, λ_{pPs} is the annihilation rate of para-Ps (we do not distinguish p-Ps either in a bubble state or not), λ_{po} is the pick-off annihilation rate of Ps in a bubble state and λ_S is the o-Ps annihilation rate in free volume elements of frozen regions. However, by now experimental data were deconvoluted into three exponents. So we used the following expression to describe the long-lived component τ_3 of the spectra:

$$\frac{1}{\tau_3} = \lambda_S \frac{n_v(0)}{n_v(0) + n_{oPs}(0)} + \lambda_{po} \frac{n_{oPs}(0)}{n_v(0) + n_{oPs}(0)}. \quad (3)$$

Implicitly two temperature dependent quantities, λ_v and λ_b , enter this expression. It is reasonable to describe them by the Arrhenius-like law $\lambda_{v,b}(T) \sim \exp(-E_{v,b}/T)$ and extract corresponding activation energies for free volume elements E_v and premelted regions E_b .

Fitting the model (3) to the experimental data (Fig. 2) in the range close to melting points, we obtain temperature dependencies of trapping rates, Fig. 3. To eliminate correlation of parameters in the Arrhenius law the following procedure was applied. Melting is assumed to occur when the number of premelted regions (let a typical size of these regions is R_S) allows to fill the whole space, i.e. $\lambda_b(T = T_m) / [4\pi D R_S] \cdot \frac{4}{3}\pi R_S^3 = 1$. From this relation it is possible to get an additional constraint for $\lambda_b(T = T_m)$. Furthermore, if we consider the energy E_b as an energy necessary for melting of the media inside a premelted domain

$(\frac{4}{3}\pi R_S^3)$, then $E_b = q_m \cdot \frac{4}{3}\pi R_S^3 \cdot \rho_S$. Thus obtained relations for E_b and $\lambda_b(T = T_m)$ are dependent on the only parameter R_S which has a meaning of geometrical size of homogeneously distributed volumes responsible for melting.

As a result of fitting we obtain activation energies which are as follows:

substance	methanol	ethanol	butanol	water
E_v , [eV]	1	0.9	0.8	2.5
E_b , [eV]	3.5	2.9	7.2	Not used

According to experimental data (Fig. 2), water doesn't indicate any significant influence of premelting on positronium lifetime especially before its melting point, therefore for it we assumed $\lambda_b = 0$.

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